

Claims:

1. A method for the preparation of a supported catalyst composition suitable for the oxidation of ethane to ethylene and/or acetic acid, and/or the oxidation of ethylene to acetic acid, said supported catalyst composition comprising a catalyst comprising one or more metal components, supported on a support comprising alpha-alumina, which
5 method comprises:
 - (a) forming a slurry of the one or more metal components and alpha-alumina support particles or an alpha-alumina support precursor; and
 - (b) spray-drying the slurry.
2. The method according to claim 1, which further comprises:
10 (c) calcining the spray-dried slurry.
3. The method according to claim 1 or claim 2, wherein the alpha-alumina used for the support has a surface area, as measured by BET, of less than $15 \text{ m}^2/\text{g}$, such as less than $10 \text{ m}^2/\text{g}$, for example, less than $5 \text{ m}^2/\text{g}$.
4. The method according to any one of the preceding claims, wherein the alpha-
15 alumina used for the support has a surface area, as measured by BET, of at least $0.1 \text{ m}^2/\text{g}$, most preferably at least $0.5 \text{ m}^2/\text{g}$, such as in the range $0.5 \text{ m}^2/\text{g}$ to less than $10 \text{ m}^2/\text{g}$, more preferably in the range $0.5 \text{ m}^2/\text{g}$ to less than $5 \text{ m}^2/\text{g}$.
5. The method according to any one of the preceding claims, wherein the alpha-alumina used for the support has a density of between 0.5 and 5 g/cc , preferably between
20 0.8 and 2 g/cc .
6. The method according to any one of the preceding claims, wherein the support is alpha-alumina.

7. The method according to any one of claims 1 to 5, wherein the support comprises a mixture of alpha-alumina with one or more non-alpha-alumina materials.

8. The method according to claim 7, wherein the support comprises one or more alpha-aluminas in combination with one or more silicas and wherein the one or more silicas are low sodium-containing silicas.

9. The method according to claim 7 or claim 8, wherein alpha-alumina comprises at least 10% by weight of the total support, preferably at least 20%, such as 40% or more, and most preferably 50% or more by weight of the total weight of the support.

10. The method according to any one of the preceding claims, wherein the supported catalyst composition has a surface area, as measured by BET, of between 0.1 and 20 m²/g, more preferably between 1 and 5 m²/g.

11. The method according to any one of the preceding claims, wherein the supported catalyst composition has a density of between 0.5 and 5g/cc, more preferably between 0.8 and 2 g/cc.

12. The method according to any one of the preceding claims, wherein the one or more metal components are present in the supported catalyst composition in a total amount equivalent to between 5% and 60% by weight of the total supported catalyst composition, preferably between 20 and 50% inclusive by weight.

13. The method according to any one of the preceding claims, wherein the catalyst comprises, as a metal component, palladium.

14. The method according to claim 13, wherein the catalyst is represented by the formula Mo_aPd_bX_cY_d wherein X represents one or several of Cr, Mn, Nb, Ta, Ti, V, Te and W; Y represents one or several of B, Al, Ga, In, Pt, Zn, Cd, Bi, Ce, Co, Rh, Ir, Cu, Ag, Au, Fe, Ru, Os, K, Rb, Cs, Mg, Ca, Sr, Ba, Nb, Zr, Hf, Ni, P, Pb, Sb, Si, Sn, Tl and U and a=1, b=0.0001 to 0.01, c = 0.4 to 1 and d = 0.005 to 1.

15. The method according to any one of the preceding claims, wherein the catalyst comprises the metals molybdenum, vanadium and niobium.

16. The method according to any one of claims 1 to 12, wherein the catalyst comprises the metals molybdenum, vanadium, niobium and gold in the absence of palladium according to the empirical formula :



wherein Y is one or more metals selected from the group consisting of : Cr, Mn, Ta, Ti,

B, Al, Ga, In, Pt, Zn, Cd, Bi, Ce, Co, Rh, Ir, Cu, Ag, Fe, Ru, Os, K, Rb, Cs, Mg, Ca, Sr, Ba, Zr, Hf, Ni, P, Pb, Sb, Si, Sn, Tl, U, Re, Te and La;

a, b, c, d, e and f represent the gram atom ratios of the metals such that :

$$0 < a \leq 1; 0 \leq b < 1 \text{ and } a + b = 1;$$

5 $10^{-5} < c \leq 0.02;$

$$0 < d \leq 2;$$

$$0 < e \leq 1; \text{ and}$$

$$0 \leq f \leq 2.$$

17. The method according to claim 16, wherein $a > 0.01$, $d > 0.1$ and $e > 0.01$.

10 18. The method according to claim 17, wherein $e \leq 0.5$ and $0.01 \leq f \leq 0.5$.

19. The method according to claim 18, wherein $0.4 \leq d \leq 0.865$; $0.135 \leq e \leq 0.23$; and $0.55 \leq d + e \leq 1$;

20. The method according to claim 19, wherein $a > 0.01$, $0.0001 < c \leq 0.002$, $0.425 \leq d \leq 0.8$, $0.14 \leq e \leq 0.20$, $0.6 \leq d + e \leq 0.95$, and $f \leq 0.2$.

15 21. The method according to claim 20, wherein $0.0005 < c \leq 0.001$, $0.45 \leq d \leq 0.7$, $e \geq 0.15$, $d + e \leq 0.9$, and $f \leq 0.02$.

22. The method according to claim 21, wherein $d \geq 0.5$, $e \leq 0.18$, and $d + e \geq 0.7$.

23. The method according to claim 22, wherein $d + e \geq 0.8$.

24. The method according to any one of claims 16 to 23, wherein $a = 1$.

20 25. The method according to any one of claims 16 to 24, wherein Y is selected from the group consisting of Sn, Sb, Cu, Pt, Ag, Fe and Re.

26. The method according to any one of the preceding claims, wherein step (a) comprises (i) preparing separate solutions comprising each metal component by dissolving sufficient quantities of soluble compounds and/or dispersing any insoluble
25 compounds or quantities of said compounds so as to provide a desired gram-atom ratio of the metal components in the catalyst composition, (ii) where the catalyst comprises more than one metal component, mixing the respective solutions to form a single solution comprising the desired quantities of metal components, and (iii) mixing the resulting solution with alpha-alumina support particles or alpha-alumina precursor, and
30 if required, other support materials or precursors, to form a slurry.

27. The method according to claim 26, wherein the one or more solutions comprising the metal components are aqueous solutions having a pH in the range from 1

to 12, preferably from 2 to 8, at a temperature of from 20° to 100°C.

28. The method according to any one of the preceding claims, wherein the spray-drying is performed at an outlet temperature of at least 100°C, preferably between 120°C and 180°C, for example, between 130°C and 150°C

5 29. The method according to any one of the preceding claims, wherein the spray-drying is performed at an inlet temperature of between 250°C and 350°C, for example, between 280°C and 300°C.

30. A supported catalyst composition suitable for the oxidation of ethane to ethylene and/or acetic acid, and/or the oxidation of ethylene to acetic acid, characterised in that
10 the supported catalyst composition has been prepared according to the method of any one of claims 1 to 29.

31. A process for the selective oxidation of ethane to ethylene and/or acetic acid, and/or the selective oxidation of ethylene to acetic acid which oxidation process comprises contacting ethane and/or ethylene with a molecular oxygen-containing gas at
15 elevated temperature in the presence of a spray-dried supported catalyst composition as claimed in claim 30.

32. The process according to claim 31, wherein the supported catalyst composition has been calcined by heating at a temperature in the range from 250 to 500°C in the presence of an oxygen-containing gas, for example air.

20 33. The process according to claim 31 or claim 32 which is a fluidised bed process.

34. The process according to claim 33, wherein the particle size of the supported catalyst composition is such that at least 50% of the particles have a size less than 300 microns, and preferably such that at least 90% of the particles have a size of less than 300 microns.

25 35. The process according to claim 34, wherein the supported catalyst composition is in the form of microspheroidal particles.

36. The process according to any one of claims 31 to 35, wherein the molecular oxygen-containing gas is oxygen or oxygen diluted with a suitable diluent, such as nitrogen.

30 37. The process according to any one of claims 31 to 36, wherein there is fed, in addition to ethane and/or ethylene and the molecular oxygen-containing gas, water (steam).

38. The process according to any one of claims 31 to 37, wherein there is fed to the process a feed composition (in mol%) comprising 40 to 80% ethane, 0 to 10% ethylene, 0 to 20% water, 2 to 10% oxygen and with a balance of inert gas, preferably nitrogen.

39. The process according to any one of claims 31 to 38, wherein the elevated
5 temperature is in the range from 200 to 500°C, preferably from 200 to 400°C, and most preferably in the range of 260°C to 360°C.

40. The process according to any one of claims 31 to 39, wherein the process is operated at a pressure is in the range from 1 to 50 bar, preferably from 1 to 30 bar.

41. The process according to any one of claims 31 to 40, wherein the process is
10 operated with a gas hourly space velocity (GHSV) of between 100 and 10,000 h⁻¹, preferably 1000 to 5000 h⁻¹.

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